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NO_x Storage and Reduction over Copper-based Catalysts.

Part 1: BaO + CeO₂ Supports.

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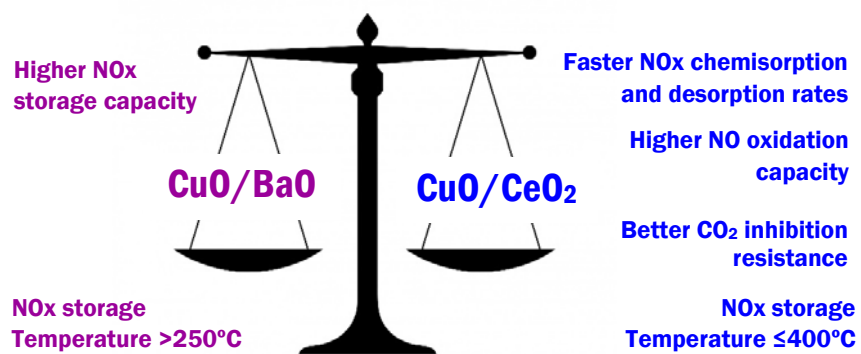
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Graphical abstract



Highlights

- CuO/CeO₂ chemisorbs NO_x at T≤400°C, and stored nitrate/nitro decompose above 400°C
- CuO/BaO chemisorbs NO_x at T>250°C; low-temperature NO oxidation was very low
- NO_x chemisorption and desorption rates were faster for CuO/CeO₂ than for CuO/BaO
- H₂ was more effective than CO as NSR reductant for all CuO/(CeO₂ and/or BaO) catalysts
- CuO/CeO₂ showed the best resistance to deactivation upon high frequency CO pulses

Abstract

The performance of noble metal-free copper-based NSR catalysts was studied by rapid-scan *operando* DRIFTS, using CeO₂, BaO and BaO + CeO₂ mixtures with different ratios as supports. The maximum temperature for CuO/CeO₂ utilization as NSR catalyst was 400°C, as the stored NO_x species decomposed above this temperature. At 400°C, CuO/CeO₂ showed high NO oxidation capacity and NO_x were stored on the catalyst mainly in the form of nitrates and lower populations of nitro groups. CuO/BaO was not suitable for NSR below 250°C, because its oxidation activity was very low and its NO_x storage capacity was negligible, but it did not exhibit upper temperature restrictions until 500°C. The effect of temperature on NO_x chemisorption on copper catalysts with BaO + CeO₂ mixed oxide supports was between those of CuO/CeO₂ and CuO/BaO. NSR experiments performed with high frequency H₂ or CO pulses (micropulses every 120, 60 or 30 seconds) at 400°C showed that regeneration with H₂ was more effective than with CO, and this was attributed to the higher reactivity of H₂ rather than to the poisoning effect of the reaction products (H₂O and CO₂ respectively). Nitrates were the main form of chemisorbed nitrogen oxides on all catalysts in NSR experiments at 400°C, and NO_x chemisorption and desorption rates were faster for CuO/CeO₂ than for CuO/BaO. The general behavior of all catalysts tested for NSR at 400°C was quite similar, and only certain differences were observed during the highest frequency pulses of CO, where CuO/CeO₂ showed the best resistance to deactivation. For all catalysts, N₂ was the only NO_x reduction product detected during H₂ regeneration.

Keywords: NSR; deNO_x; diesel aftertreatment; copper catalyst; Ceria; Barium oxide; DRIFTS; Operando.

1.- Introduction.

Diesel engine exhausts are net oxidizing, and NO_x reducing under such unfavorable conditions is a current challenge of ongoing research. The NO_x Storage and Reduction (NSR) strategy is one of the options for NO_x removal from diesel exhausts, which operates under cyclic oxidizing and reducing conditions [1-4]. A typical NSR catalyst includes a basic oxide that chemisorbs NO_x under normal running conditions, and periodically, a reductant is fed to the exhaust that desorbs and reduces the stored NO_x. Barium oxide is the most studied basic oxide for NSR catalysts. Pt is also included in the catalyst formulation to accelerate NO oxidation to NO₂, hence improving NO_x chemisorption, and to catalyze further reduction [4]. The most convenient reductants for NSR would be hydrocarbons, because fuel is already on board. However, their reactivity is usually not high [5] and CO + H₂ mixtures are more suitable [6], and these can be produced on board by steam reforming, water gas shift reaction, partial oxidation, or autothermal reforming [4].

It has been recently reported that the NSR behavior of Ba–Pt/Al₂O₃ catalyst is improved by addition of ceria, because ceria enhances the NO_x storage capacity and the NO oxidation activity [7]. It has been also observed that addition of ceria to Pt–Ba/Al₂O₃ catalysts has a positive effect on NO_x reduction with H₂, because it lowers the thermal threshold for hydrogen activation. The utilization of CeO₂ [8,9] or CeZr mixed oxides [9,10] instead of Al₂O₃ as Pt + BaO supports has been also studied for NSR application, and also barium-free Pt/Ce_xPr_{1-x}O₂ catalysts [11].

The potential of noble metal-free NSR catalysts has not been studied in detail in the literature, and this is one of the goals of the current study. This would have practical relevance to lower the price of the catalysts and to decrease the dependence of noble metals. Vijay et al. [12] found that a noble metal-free Co–Ba catalyst was able to store NO_x as efficiently as a Pt–Ba NSR catalyst, and Palomares et al. [13] reported that Mg/Al

hydrotalcites containing copper or cobalt are active for low temperature NSR, and that an optimum formulation with Co/Mg/Al = 15/60/25 outperformed a reference Pt–Ba/Al₂O₃ catalyst. The promoting effect of CuZSM-5 to the NSR activity of Pt–Rh/Ba/Al₂O₃ was also demonstrated [14], and the promising behavior of copper-containing SrTiO₃ perovskite as NSR catalyst has been reported [15]. In these NSR catalysts, copper improves the NO oxidation capacity and NO_x are stored on the mixed oxide.

This article is the first in a series devoted to the study of noble metals-free copper catalyst for NSR. In this article, the effect of CeO₂, BaO and BaO+CeO₂ supports on the NSR behavior of copper has been studied by *operando* DRIFTS-MS-Chemiluminiscence, paying special attention to the reaction mechanism. Realistic periods of lean operation (30-120 seconds) similar to those originally proposed by Toyota in the mid 90s [16] and periodic micropulses of reductant were used. This detail is significant when making comparison with other studies because, as has been highlighted by other authors [17], despite the high level of activity in this area, it is surprising that most studies have been conducted with much longer lean periods and regeneration times, which are far from realistic conditions. Rapid-scan *operando* DRIFTS experiments were performed in a spectrometer that is able to obtain up to 17 spectra per second. This novel methodology has recently demonstrated to be very powerful to study the NSR reaction when performed with high frequency micropulses [18].

Further articles in this series will be devoted to the study of the effect of Zr, La, Pr and Nd dopants on the NSR performance of CuO/CeO₂ NSR catalysts, and on the simultaneous removal of NO_x and soot with Pr-doped CuO/CeO₂ under NSR conditions.

2.- Experimental details

2.1. Catalysts preparation

$x\text{BaO} + (1-x)\text{CeO}_2$ supports were prepared with $x = 1, 0.8, 0.6, 0.4, 0.2$ and 0 with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa-Aesar, 99.5 %) and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Panreac) as Ce and Ba precursors, respectively. Aqueous dissolutions of the Ce and Ba precursors were prepared with 10 ml of solvent, using the required amounts to obtain 5 g of each mixed oxide. The dissolutions were introduced in a muffle furnace previously heated at 200°C , and after 1 hour, the temperature was increased at $10^\circ\text{C}/\text{min}$ until 500°C , holding the samples at this temperature for 2 hours. The nomenclature used for the $x\text{BaO} + (1-x)\text{CeO}_2$ supports is “ $x\text{BaO}-(1-x)\text{CeO}_2$ ” where x and $(1-x)$ are the percentages of BaO and CeO_2 , respectively.

$\text{CuO}/(x\text{BaO}-(1-x)\text{CeO}_2)$ catalysts were prepared with a 5 wt. % target Cu loading. The required amount of $\text{Cu}(\text{NO}_3)_2 \cdot 5 \cdot (1/2)\text{H}_2\text{O}$ (Sigma Aldrich, 98 %) was dissolved in 2 ml of water and 2.5 grams of each $(x\text{BaO}-(1-x)\text{CeO}_2)$ support was impregnated with this solution. The impregnated supports were heat treated following the same protocol used for the supports preparation, that is, they were introduced in a muffle furnace previously heated at 200°C , and after 1 hour, the temperature was increased at $10^\circ\text{C}/\text{min}$ until 500°C , holding this temperature for 2 hours.

2.2. Catalyst characterization

The catalysts were characterized by XRD and by N_2 adsorption at -196°C . X-Ray diffractograms were recorded from 10 to $90^\circ 2\theta$ in a Bruker D8 advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda=0.15418$ nm). N_2 adsorption isotherms were obtained at -196°C in an automatic volumetric system (Autosorb-6, Quantachrome) after the catalysts were degassed at 150°C for 4 hours.

2.3. NO_x chemisorption and NSR experiments

NO_x chemisorption and NSR performance were studied in a Fourier Transform Infrared Spectrometer Shimadzu (IR Tracer-100) with a Harrick reaction cell coupled to a EcoSys-P mass spectrometer and a chemiluminescence NO_x analyzer (Thermo 42H). The sample holder of the DRIFT cell was 6.3 mm diameter with a height of 3.3 mm which was filled with sample (100 mg in the absence of diluent). It is important to note that the infrared spectrum only provides information on the top < 0.2 mm of this sample [19].

The reaction cell was designed to allow the reaction gas mixture (50 ml/min; 850 ppm NO_x + 5% O₂ + N₂) to pass through the catalyst bed with the gas exit underneath.

It is worth mentioning that temperature control and determination in DRIFTS cells is problematic. It has been reported that the actual temperature of the catalyst bed can be significantly lower than the set temperature, with differences of around 50°C when operating at 400°C [20]. This must be kept in mind when cross referring to data obtained using other devices including reactors.

Three types of experiments were carried out: Temperature programmed NO_x storage experiments, isothermal NO_x storage at 400°C and Isothermal NO_x Storage and Reduction (NSR) at 400°C.

In temperature programmed NO_x storage experiments, a background spectrum of the catalyst was recorded at room temperature, and the NO_x/O₂/N₂ mixture was fed to the DRIFTS cell. After 15 min, the temperature was increased at 10°C/min until 500°C and DRIFT spectra and chemiluminescence NO_x measurements were simultaneously recorded. 40 scans were averaged to obtain each spectrum, which were measured in the 4000-1000 cm⁻¹ range at 4 cm⁻¹ resolution.

In isothermal NO_x storage experiments at 400°C, the temperature was increased from room temperature to 400°C under N₂. A background spectrum of the catalyst was recorded at 400°C, and then the inert gas was replaced by the NO_x/O₂/N₂ mixture, considering this as time = 0 min. DRIFT spectra and chemiluminescence NO_x measurements were simultaneously recorded with time until saturation of the catalysts. In these experiments, the settings used to obtain the spectra were the same as in previous temperature programmed NO_x storage experiments.

Isothermal NO_x storage and reduction (NSR) experiments were carried out following the protocol described for isothermal NO_x storage experiments at 400°C, but in addition, 100 µl pulses of CO or H₂ were fed with frequencies of 120, 60 or 30 seconds. These times are in the range of realistic values for application of the NSR technology, as developed by Toyota [16,17,21]. In these experiments, the DRIFT spectrometer was operated in the rapid-scan mode, and one spectrum was recorded per second as an average of 7 scans, which were recorded with a resolution of 8 cm⁻¹ in the 4000-1000 cm⁻¹ range. The Rapid-scan Software (Shimadzu Corporation) was used to handle the large volume of data generated. The gas composition was monitored during these experiments with the mass spectrometer. This technique was used in preference to chemiluminescence because the sampling frequency of the mass spectrometer was much faster. Previous comparison of the NO_x concentrations measured by chemiluminescence and mass spectrometry (m/z 30) confirmed that both techniques provided comparable results. The benefit of chemiluminescence is that it is able to distinguish between NO and NO₂ while the m/z 30 signal shows the NO_x sum (i.e. NO + NO₂).

3.- Results and discussion

3.1. Catalysts characterization

X-Ray diffractograms of the catalysts were compiled in Figure 1, along with the cell parameter of the fluorite phase of ceria, calculated from these diffractograms, together with the BET surface areas calculated from the N₂ adsorption isotherms. The diffractogram of the CuO/CeO₂ catalyst showed the peaks of fluorite, which is the cubic phase of ceria, and evidence of CuO peaks were not observed on this catalyst indicating high dispersion. On the contrary, CuO peaks were identified in all barium-containing catalysts, and this indicated that copper was more poorly dispersed. This is consistent with the decrease of the BET surface area of the catalysts (Table 1) by increasing the BaO loading, which decreases from 60 m²/g for the CuO/CeO₂ catalyst to 1 m²/g for CuO/BaO. The diffractogram of CuO/BaO is complex and included peaks of several barium species such as BaO, BaCO₃ and Ba(OH)₂, and the catalysts with (xBaO-(1-x)CeO₂) supports show features of both CuO/BaO and CuO/CeO₂. The cell parameter values of the fluorite phase of ceria included in Table 1 were quite similar for all samples, and were consistent with typical reference values obtained with pure ceria [22], suggesting limited or no insertion of barium cations into the ceria framework.

In conclusion, these characterization suggested that the (xBaO-(1-x)CeO₂) supports consisted of a mixture of oxides, carbonates and hydroxides that did not form solid solutions. The surface area of CeO₂ was much higher than that of BaO, and (xBaO-(1-x)CeO₂) mixed oxides had surface areas that decreased with the BaO content. This affected CuO dispersion, which was much better on CeO₂ than on barium-containing supports.

3.2. Temperature programmed NO_x storage experiments

Temperature programmed experiments were performed and the copper catalysts studied, once in contact with the NO_x/O₂/N₂ gas flow, chemisorbed NO_x and accelerated the oxidation of NO to NO₂. Figure 2 shows (a) the NO_x concentration and (b) the percentage of NO₂ with regard to total NO + NO₂ monitored with the chemiluminiscence NO_x analyzer during the temperature programmed NO_x storage experiments.

Different ranges of temperatures could be distinguished considering the NO_x profiles (Figure 2a). NO_x concentrations below the inlet level were detected for CuO/(xBaO-(1-x)CeO₂) catalysts with $x \leq 60\%$ at temperatures below 200°C. That is, these catalysts removed NO_x from the gas mixture in this range of temperatures. Note that the catalysts were in contact with the NO_x/O₂/N₂ mixture for 15 minutes at room temperature, and NO_x was also adsorbed on the catalysts during this period of time. On the contrary, the barium-rich CuO/BaO and CuO/(80BaO-20CeO₂) catalysts did not store NO_x at low temperature, and therefore, it was concluded that the presence of cerium was necessary for the catalysts to store NO_x below 200°C. This could be related to the very low surface area of these two catalysts (1 m²/g; Table 1), which was too low to adsorb significant amounts of NO_x.

The catalysts that stored NO_x below 200°C (CuO/(xBaO-(1-x)CeO₂ with $x \leq 60\%$) released NO_x in the range 200-300°C, indicating low thermal stability of the species adsorbed at low temperature, and CuO/CeO₂ additionally released NO_x above 300°C. All barium-containing catalysts chemisorbed NO_x above 300°C but, while catalysts with cerium contents in the $20\% \leq x \leq 60\%$ range released NO_x above 450°C, CuO/BaO and CuO/(80BaO-20CeO₂) continued to chemisorb until the maximum temperature of the experiments (500°C).

The catalytic oxidation of NO to NO₂ took place simultaneously during NO_x chemisorption/desorption (Figure 2). NO₂ is the most thermodynamically stable nitrogen

oxide at room temperature, but the oxidation of NO is kinetically restricted and requires long times for NO to become oxidized to NO₂ in the absence of catalyst. NO₂ was present at 20-25 % at room temperature for all experiments, and it was experimentally confirmed that this was the amount of NO converted to NO₂ in the experimental set-up without catalyst participation.

CuO/CeO₂ was the most active catalyst for NO oxidation to NO₂, with an onset NO₂ release temperature of 100°C under the experimental conditions employed. This is consistent with the conclusions of Pereda-Ayo et al. [7], who reported that ceria improved the NO oxidation capacity of model Ba-Pt/Al₂O₃ catalysts, and this enhanced the NO_x storage capacity of the catalysts. The NO₂ curve obtained with CuO/CeO₂ (Figure 2b) decreased above 175°C, and this is not attributed to the decrease of the NO oxidation capacity of CuO/CeO₂ (reaction rate increases with temperature) but to the desorption of NO_x stored at lower temperature (compare Figures 2a and 2b). Considering typical experimental conditions used in fixed-bed reactors [23] it would be expected that the NO₂ percentage should increase with temperature until the thermodynamic limitation is achieved, and above this temperature, the NO₂ profile should follow the thermodynamically predicted curve. The high temperature part of the expected curve was observed in Figure 2b, and the NO₂ percentage followed the values defined by thermodynamic equilibrium above 400°C, but part of the NO₂ curve was absent between 170 and 450°C. The difference in the NO₂ profile observed in the DRIFTS cell and in previous experiments performed in a fixed-bed reactor [23] was the space velocities employed, being much lower in the DRIFTS cell. For this reason, the effect of NO_x desorption in the NO₂ profiles was minor or negligible for experiments performed under the experimental conditions typically used in fixed-bed reactors, but not for those used in the DRIFTS cell.

With the exception of CuO/CeO₂, the remaining catalysts showed very low NO oxidation capacity (Figure 2b), with onset NO₂ release temperatures above 300°C, and this could be related to the poor copper dispersion. For most catalysts, NO_x chemisorption and NO₂ formation were coupled, that is, NO_x chemisorption started at 300°C (Figure 2a), once NO₂ was detected in the gas phase due to catalytic oxidation of NO (Figure 2b). This was not surprising because NO₂ is usually chemisorbed more readily than NO [24], and NSR catalysts typically chemisorb NO_x to a greater extent once the temperature is high enough for catalytic oxidation of NO to take place.

As a summary of NO oxidation and storage results (Figures 2a and 2b), it can be concluded that CuO/CeO₂ was much more effective than CuO/BaO for NO_x storage and NO oxidation at low temperature, but the stored species were less stable, being desorbed above 200°C. On the contrary, CuO/BaO required higher temperatures for NO_x chemisorption than CuO/CeO₂ but the stored species remained stable until 500°C (at least). The behaviour of CuO/(xBaO-(1-x)CeO₂) catalysts was in between, with catalysts of high barium concentration behaving more similarly to CuO/BaO while those with high cerium concentration showed more commonality with CuO/CeO₂.

The adsorbed NO_x species on the catalysts were monitored by DRIFTS during temperature programmed NO_x storage experiments. As representative examples of the spectra obtained, data for CuO/CeO₂ and CuO/BaO are shown in Figure 3a and 3b, respectively and the spectra of the remaining catalysts are included in the supplementary material (Figure 1SM). In all sets of spectra, bands attributed to nitrogen-containing species grew with increasing temperature while carbonate bands decreased as nitrogen oxides replaced carbonates. This general observation can be extended to all catalysts with (xBaO-(1-x)CeO₂) supports (not shown for sake of brevity). The possibility of cleaning the catalysts surface before conducting experiments by removing carbonates with a

thermal treatment was explored. Carbonate removal was possible for CuO/CeO₂, but not for barium-rich catalysts due to the very high temperatures required which might also have modified catalysts characteristics and may have been beyond the limit of the temperature maxima of the DRIFTS cell. For this reason, the presence of carbonates on all catalysts which would be formed upon exposure to atmospheric CO₂ was assumed. This has some practical significance as carbonates will always be present under real NSR operation conditions, and there has been debate regarding the role of carbonates on the performance of Pt/BaO/Al₂O₃ model NSR catalysts [25] that justifies the study of carbonated samples.

Before discussing the behaviour of the different bands of nitrogen species observed in Figure 3 in detail, it is worth mentioning that it has been recently reported that the molar absorption coefficients of the overlapping bands due to carbonates and nitrates are not identical. For this reason, the true position of the nitrate and nitrite bands cannot be assessed from such complex spectra [26, 27]. However, despite this limitation, some general conclusions can be reached while bearing in mind that the position of the nitrite and nitrate bands in the following discussion may differ to some extent from those described for other carbonate-free systems.

Nitrates show three bands in the 1650-970 cm⁻¹ range, and the position of these bands depends on the surface to which they are anchored and on the bonding arrangement with the surface (monodentate (M-O-NO₂), bidentate (M-O₂NO) or bridging ((M-O)₂=NO), M being a metal cation) [28]. In the spectra obtained with the CuO/CeO₂ catalyst (Figure 3a), nitrate bands appeared at 1545, 1235 and 1010 cm⁻¹, and are consistent with the presence of monodentate or bidentate nitrates. This catalyst also showed a band at 1415 cm⁻¹ that could be assigned to nitro groups (M-NO₂) and, at low temperatures, a band at 1190 cm⁻¹ that could be attributed to bridging nitrites ((M-O)₂=N).

In addition, evidence of carbonate depletion was observed in this wavenumber range. The antisymmetric and symmetric stretching modes of the terminal CO bonds in poly or mono-dentate carbonates usually appear around 1480 and 1350 cm^{-1} , respectively [29], and these features were observed in the spectra of CuO/CeO₂.

The CuO/BaO catalyst (Figure 3b) did not show evidence of nitro groups, but instead, features at 1535 and 1280 cm^{-1} could be attributed to nitrates, probably in monodentate configuration, and as bridging nitrites at 1225 cm^{-1} at low temperatures. In this case, the depletion of carbonates also had a strong influence on the spectra in the 1500-1300 cm^{-1} range.

Quantitative analysis of the spectra was hindered due to the depletion of carbonate species which led to diminishing band intensities while those of the nitrogen oxide groups were simultaneously increased. The intensity of the band due to nitrites appearing around 1225-1190 cm^{-1} can be properly estimated without significant influence by carbonates, and the values obtained were plotted as a function of temperature (Figure 4a) after baseline correction. The absorbance at 1280-1235 cm^{-1} was selected for monitoring nitrates (Figure 4b), but in this case the possibility that data are partially masked by carbonate depletion in some spectra cannot be ruled out. These data where evidence of interference due to carbonates is apparent are plotted in Figure 4 with dashed lines and open symbols.

Nitrites were progressively accumulated on CuO/CeO₂ from room temperature until *ca* 150°C, and above this temperature their concentration decreased, consistent with the release of NO_x observed above this temperature (Figure 2a). The concentration of nitrates on CuO/CeO₂ (Figure 4b) increased with temperature until 300°C, with depletion only observed above 400°C, in accordance with the release of NO_x at high temperature (Figure 2a). However, evidence of nitrate depletion was not observed in the 150-300°C

range. This suggests that there are two mechanisms by which NO_x is chemisorbed on CuO/CeO₂. Adsorption of NO_x at low temperature results in the formation of nitrites that decompose in the 150-300°C range. The formation of nitrates is favored at higher temperature, which is in accordance with the increase in the catalyst oxidation capacity (Figure 2b), and nitrates remained stable on the catalyst until 400°C. This behavior is confirmed in data presented in Figure 4c, where the ratio between the absorbance of the nitrite and nitrate bands is shown as a function of temperature. The nitrite/nitrate ratio on the CuO/CeO₂ catalyst decreased from room temperature until 250°C and remained stable above this temperature.

The evolution of the nitrogen oxide species chemisorbed on CuO/BaO followed a different pattern. The amount of nitrites and nitrates accumulated on CuO/BaO below 200°C was much lower than that observed on CuO/CeO₂, and this was in agreement with the NO_x profiles (Figure 2a). The CuO/BaO catalyst chemisorbed detectable amounts of NO_x above 250°C (Figure 2a), and above this temperature, surface nitrites disappeared (Figure 4a). This suggested that the increased chemisorption above this temperature was related to the formation of nitrates, although unfortunately, this could not be confirmed by DRIFTS (Figure 4b) due to carbonates interference. The slight increase of the NO₂ concentration observed above 200°C (Figure 2b) suggested that the CuO/BaO catalyst was able to oxidize NO above this temperature, and surface nitrites were simultaneously oxidized to surface nitrates. Once this occurs, the NO_x chemisorption capacity of CuO/BaO increases.

As a summary of the temperature programmed NO_x storage experiments, it can be concluded that, for the purpose of the NSR technology, the maximum operating temperature for CuO/CeO₂ is 400°C, because the stored NO_x species decompose above this threshold. At 400°C, CuO/CeO₂ showed high oxidation capacity (the NO₂ profile

reached the thermodynamic equilibrium under the experimental conditions of this study) and NO_x was stored on the catalyst mainly in the form of nitrates. On the contrary, CuO/BaO is not suitable for NSR below 250°C, due to its low oxidation activity and its negligible NO_x storage capacity. However, CuO/BaO did not exhibit temperature restrictions until 500°C, which was the maximum temperature employed in this study. Finally, the behavior of catalysts with (xBaO-(1-x)CeO₂) supports was between those described for CuO/CeO₂ and CuO/BaO. These conclusions lead us to select 400°C for further assessment of the NSR process under isothermal conditions.

3.3. Isothermal NO_x storage at 400°C.

Figure 5 compiles the NO_x removal profiles obtained with the different catalysts at 400°C and Table 2 the amounts of NO_x stored. These quantitative results were determined using the chemiluminiscence analyser.

The highest NO_x storage capacity was obtained with CuO/BaO (1204 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$), the lowest corresponded to CuO/CeO₂ (168 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$), and the performance of catalysts with (xBaO-(1-x)CeO₂) supports was between those of CuO/CeO₂ and CuO/BaO (281-437 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$). The amounts reported in the literature for reference catalysts are, for example, 324 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$ for 1%Pt–20%Ba/Al₂O₃ [30] and 714 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$ for a 1%Pt–10%Ba/Al₂O₃ [31] also at 400°C. These values indicate that CuO/CeO₂ presents lower NO_x storage capacity than the reference materials, which is reasonable given that (i) the NO oxidation capacity of Pt is higher to that of CuO (and NO₂ is chemisorbed better than NO) and (ii) the NO_x storage capacity of ceria is lower than that of BaO/BaCO₃. On the other hand, CuO/BaO

attains higher NO_x storage amounts than the reference materials because BaO was not diluted with alumina.

DRIFTS obtained with CuO/CeO₂ and CuO/BaO during the isothermal NO_x storage experiments are compiled in Figure 6a and Figure 6b, respectively. After a few minutes under reaction conditions, CuO/CeO₂ showed three bands at 1540, 1220 and 1010 cm⁻¹, which were consistent with the presence monodentate and/or bidentate nitrates. A poorly defined band was also observed at 1400 cm⁻¹ that could be ascribed to nitro groups. This behavior was consistent with the conclusions of the temperature programmed experiments, and confirmed that the good oxidation capacity of the CuO/CeO₂ catalyst leads to the storage of oxidized nitrogen oxide species. Note that the oxidation state of nitrogen in NO, which is the main nitrogen oxide on the gas fed, is +2 while the oxidation state in the stored species is +4 (nitro groups) and +5 (nitrates). The spectra obtained with CuO/(20BaO-80CeO₂), CuO/(40BaO-60CeO₂) and CuO/(60BaO-40CeO₂), (not shown for the sake of brevity), were qualitatively similar to those of Cu/CeO₂, with monodentate and/or bidentate nitrate bands at 1550-1545, 1260-1250 and around 1000 cm⁻¹, and the nitro band at 1390-1370 cm⁻¹. However, the relative intensity of the bands depended significantly on the sample, as will be discussed later.

The spectra obtained with CuO/BaO (Figure 6b) and CuO/(80BaO-20CeO₂) (not shown) presented more bands than those of catalysts with higher loading of ceria. In addition to the nitrate bands at 1530 and 1275 cm⁻¹, and the nitro band at 1400 cm⁻¹, these two catalysts also showed bands at 1470 and 1075 cm⁻¹ that could be attributed to monodentate nitrites. The presence of nitrites, with nitrogen in +3 oxidation state, was consistent with the lower oxidation capacity of the barium-rich catalysts with respect to those with high cerium content. This conclusion is consistent with DRIFTS studies carried out with commercial Pt-Rh/BaO/Al₂O₃ catalysts [32], where it was concluded that

NO was initially chemisorbed as nitrites on BaO. Once NO₂ was formed by NO oxidation on the noble metals, this species was chemisorbed either molecularly forming nitrates or dissociatively forming nitrites and, after a certain concentration of NO_x is accumulated on the catalyst, surface nitrites were oxidized to surface nitrates by NO₂. It has been also reported that nitrites are preferably formed on Ba-Pt/Al₂O₃ while nitrate formation is favored by addition of ceria to this catalyst due to the enhanced oxidation capacity [7].

Finally, the CuO/BaO catalyst (Figure 6b), and to a lesser extent also CuO/(80BaO-20CeO₂) (not shown), showed evidence of carbonate decomposition with a band at 1350 cm⁻¹ decreasing in intensity. This displacement of carbonates by nitrogen oxides occurred during isothermal conditions to a lesser extent than in those carried out under temperature programmed conditions, because carbonates were partially removed while heating to 400°C in inert gas.

3.4. Isothermal NO_x Storage and Reduction (NSR) at 400°C.

NO_x storage and reduction experiments were performed at 400°C with selected catalysts under the same conditions as the isothermal experiments described in the previous section, but by additionally feeding pulses of CO or H₂ at different frequencies. Figure 7 shows the m/z 30 signal followed by mass spectrometry which was used to monitor NO_x concentration during the NSR experiments.

The profile shape of the m/z 30 signal consisted of peaks that followed the frequency of the reductant pulses and are attributed to NO_x slip, that is, part of the NO_x stored on the catalyst is reduced to N₂ but a fraction is released without undergoing reduction. In practical application, operation conditions must be optimized to maximise NO_x reduction and minimise NO_x slip.

The NSR performance was mainly dependent on the nature of the reducing gas, on the pulsing frequency and, only under certain circumstances, on the nature of the copper catalyst. As a general observation, H₂ regeneration was more effective than using CO. In all cases the m/z 30 signal followed an increasing trend while exposing to CO pulses, which indicated that the catalysts were not fully regenerated by CO, and therefore, the NO_x chemisorption capacity decreased with time. On the other hand, with the exception of the first set of H₂ pulses, the m/z 30 signal followed a decreasing trend with increasing number of H₂ pulses because, in this case, the catalysts were being more fully regenerated. The difference between the efficiency of CO and H₂ became more apparent for high frequency pulses, as expected. The better regeneration capacity of H₂ with regard to CO was also reported in previous studies for Pt/Ba/Al₂O₃ catalysts [6, 33, 34].

In order to analyze the trends shown in Figure 7 in greater detail, curve fitting to the NO_x data was manually performed as shown in the example in Figure 7a (1st set of CO pulses with 120 s frequency). The NO_x concentration at the beginning of each pulse was taken for the fitting, and trend lines were obtained. These trend lines are included in Figure 8 after normalization by dividing all data corresponding to each trend line by the NO_x concentration of the first point of each series, that is, all trend lines start with a value of 1, and relative changes are shown. Also, the time scales used in Figure 8 were set by considering time = 0 min at the beginning of the first pulse of each series.

The main differences among the series of catalysts were observed during the first set of H₂ pulses (Figure 8a), where CuO/BaO loses storage capacity much more rapidly than CuO/CeO₂ and CuO/(20BaO-80CeO₂). However, the catalysts behaviour at a later stage was quite similar, except in the case where CO was pulsed at a frequency of 30 s (Figure 8h), where CuO/CeO₂ lost storage capacity slower than the other catalysts.

Catalysts regeneration was studied by rapid-scan DRIFTS. Figure 9 presents the absorbance at selected wavenumbers together with m/z signals corresponding to gas species involved in the reactions for the CuO/CeO₂ catalyst. The selected wavenumbers allow nitrates (1230 cm^{-1}) and nitro groups (1400 cm^{-1}) to be continuously monitored, the latter having marginal participation in the reactions. Additional features corresponding to nitrites or carbonate/bicarbonate species were not observed during the NSR experiment performed with CuO/CeO₂.

The m/z signals monitored during the NSR experiment carried out with CuO/BaO are compiled in Figure 10. In contrast to observations for CuO/CeO₂, the intensity of the main DRIFTS bands obtained with CuO/BaO did not follow the shape of the gas phase peaks, and for this reason are not included in Figure 10. On the contrary, broad bands were obtained, and as an example, Figure 11 shows the trend of one of the nitrate bands (at 1545 cm^{-1}) as a function of time for the complete NSR experiment. In the experiment performed using CuO/BaO, nitrite, nitro or carbonate/bicarbonate bands were also absent or negligible in intensity when compared with features due to nitrates.

The different shape of the m/z 30 curves indicates that the NO_x chemisorption and desorption rates were much faster for CuO/CeO₂ (Fig. 10) than for CuO/BaO (Fig. 11). The faster chemisorption of CuO/CeO₂ is probably linked to its higher oxidation capacity (Figure 2b) and the faster desorption rate explained on the basis of the lower stability of the chemisorbed species (see Figure 2b).

For the CuO/CeO₂ catalyst (Figure 9), the nitrate band at 1230 cm^{-1} followed a trend opposed to that of the gases pulsed, in that once H₂ or CO were introduced, the band due to nitrates decreased in intensity. The maxima of the m/z 28 signal match the nitrate band minima, confirming the release of N₂ upon catalyst surface regeneration. This was confirmed for H₂ pulses, but not for CO pulses because, in this case, both CO and N₂

contribute to the m/z 28 signal impeding the analysis of the reaction products. It is worth noting that evidence of other reduction by-products, such as N₂O (m/z 44) or NH₃ (m/z 17) were not observed under any experimental conditions.. The general trend of the nitrate band intensity depended on the reductant pulsed, in agreement with previous conclusions. The concentration of nitrates on the CuO/CeO₂ catalyst showed a net decrease upon consecutive pulses of H₂, while the opposite trend was observed using CO pulses. These general trends were more apparent when employing a pulse frequency of 30 than 120 s, consistent with the fact that these processes are relatively slow and thus are less complete as the time period is reduced. These observations confirm that H₂ was much more effective compared with CO in cleaning chemisorbed NO_x species from the catalysts.

For both catalysts studied (CuO/CeO₂ in Figure 9 and CuO/BaO in Figure 10), peaks indicating NO_x slip appeared simultaneously with the H₂O or CO₂ peaks, which are reaction products of H₂ and CO oxidation, respectively. Not all of the H₂ pulsed reacted, and the unreacted fraction also yielded H₂ peaks which appeared simultaneously with those of the NO_x and H₂O. Note that the H₂O peaks appeared delayed with respect to those of the H₂, NO_x and nitrates peaks, while CO₂ peaks were not delayed with respect to NO_x and nitrates. It was therefore concluded that H₂O interacted more strongly with the catalysts than CO₂. This may be explained on the basis that NO_x and CO₂, both compete for the same chemisorption sites on the catalyst surface, and the fed of NO_x in the gas phase hinders CO₂ chemisorption. This observation, together with the absence of carbonate/bicarbonate bands in the DRIFT spectra recorded during the NSR experiments upon CO pulses, rules out the possibility that the lower regeneration capacity of CO with regard to H₂ is related with the poisoning effect of the reaction products. On the contrary, it is suggested that H₂ regenerates the catalysts much better than CO due to its higher reactivity, as previously observed for Pt/Ba/Al₂O₃ [6].

In summary, the NSR experiments allow one to conclude that the general behavior of all catalysts tested (CuO/BaO, CuO/CeO₂ and CuO/(20BaO-80CeO₂)) was quite similar, and only certain differences were observed upon application of high frequency pulses of CO, where CuO/CeO₂ showed better resistance to deactivation than the others. In general, H₂ regeneration was more effective than CO in terms of extent of regeneration, and this was attributed to the higher reactivity of H₂ rather than to any poisoning effect of the reaction products (H₂O and CO₂, respectively). Nitrates were the main chemisorbed nitrogen oxides under the NSR experimental conditions, and NO_x chemisorption and desorption rates seemed to be faster for CuO/CeO₂ than for CuO/BaO.

4.- Conclusions.

The NSR behavior of copper catalysts was studied by operando DRIFTS-MS-Chemiluminescence, and CeO₂, BaO and BaO + CeO₂ supports were compared. The following conclusions can be drawn:

- The maximum temperature for CuO/CeO₂ application in NSR is 400°C, because stored NO_x species decomposed above this temperature. At this temperature, CuO/CeO₂ showed high NO oxidation capacity and NO_x was stored on the catalyst mainly forming nitrates and to a much lesser extent, nitro groups. On the other hand, CuO/BaO is not suitable for NSR below 250°C, because its oxidation capacity was very low and its NO_x storage capacity was negligible. However, CuO/BaO did not exhibit temperature restrictions until 500°C. The effect of temperature on the behavior of copper catalysts with BaO + CeO₂ mixed oxide supports for NO_x chemisorption was between those of CuO/CeO₂ and CuO/BaO.

- The general behavior of all catalysts tested for NSR at 400°C (CuO/BaO, CuO/CeO₂ and CuO/(20BaO-80CeO₂)) was quite similar, and only specific differences were observed when using high frequency (every 30 seconds) pulses of CO, whereby CuO/CeO₂ showed the best resistance towards the decrease in NO_x removal with time. For all catalysts, N₂ was the only NO_x reduction product detected during H₂ regeneration.
- Catalysts regeneration with H₂ was more effective than CO regeneration for NSR experiments at 400°C, and this was attributed to the higher reactivity of H₂ rather than to any poisoning effect of the reaction products (H₂O and CO₂, respectively). Nitrates were the main chemisorbed nitrogen oxide species formed on the catalyst and released under experimental conditions, and NO_x chemisorption and desorption rates were faster for CuO/CeO₂ than for CuO/BaO.

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Figure captions

Figure 1. X-Ray diffractograms of the catalysts.

Figure 2. NO_x concentration (a) and NO₂ percentage with regard to total NO + NO₂ (b) monitored with the chemiluminescence NO_x analyzer during the Temperature Programmed NO_x Storage experiments. (Gas mixture with 850 ppm NO_x + 5%O₂ + N₂).

Figure 3. Spectra obtained with CuO/CeO₂ (a) and CuO/BaO (b) and recorded during the Temperature Programmed NO_x Storage experiments. (Gas mixture with 850 ppm NO_x + 5%O₂ + N₂).

Figure 4. Absorbance of nitrite (a) and nitrate (b) bands determined from spectra on Figure 3 and nitrite to nitrate ratio (c).

Figure 5. NO_x removal with time at 400°C. (Gas mixture with 850 ppm NO_x + 5%O₂ + N₂).

Figure 6. Spectra obtained with CuO/CeO₂ (a) and CuO/BaO (b) and recorded during the Isothermal experiments at 400°C. (Gas mixture with 850 ppm NO_x + 5%O₂ + N₂).

Figure 7. NO_x concentration monitored by m/z 30 mass spectrometry signal during NO_x storage and reduction experiments performed at 400°C. (a) CuO/BaO, (b) CuO/(20BaO-80CeO₂) and (c) CuO/CeO₂.

Figure 8. NO_x data of Figure 7 fitting. NO_x concentration at the beginning of each pulse was taken for the fitting, and concentrations were normalized by dividing all data of each series by the NO_x concentration of the first point of the series. The time scales were set considering time = 0 at the beginning of the first pulse of each series. (a) H₂ pulses (1st set) 120 seconds frequency, (b) CO pulses (1st set) 120 seconds frequency, (c) H₂ pulses (2nd set) 120 seconds frequency, (d) CO pulses (2nd set) 120 seconds frequency, (e) H₂ pulses 60 seconds frequency, (f) CO pulses 60 seconds frequency, (g) H₂ pulses 30 seconds frequency and (h) CO pulses 30 seconds frequency.

Figure 9. Details of the NO_x storage and reduction experiments performed at 400°C with CuO/CeO₂. a) H₂ pulses with 120 seconds frequency, b) CO pulses with 120 seconds frequency, c) H₂ pulses with 30 seconds frequency and d) CO pulses with 30 seconds frequency. Time scale in X axis is equal to that on Figure 7c. The baseline of the m/z 28 signal has been subtracted before plotting.

Figure 10. Details of the NO_x storage and reduction experiments performed at 400°C with CuO/BaO. a) H₂ pulses with 120 seconds frequency, b) CO pulses with 120 seconds frequency, c) H₂ pulses with 30 seconds frequency and d) CO pulses with 30 seconds frequency. Time scale in X axis is equal to that on Figure 7a. The baseline of the m/z 28 signal has been subtracted before plotting.

Figure 11. Nitrates absorbance monitored by DRIFTS during NSR experiments performed at 400°C with CuO/BaO.

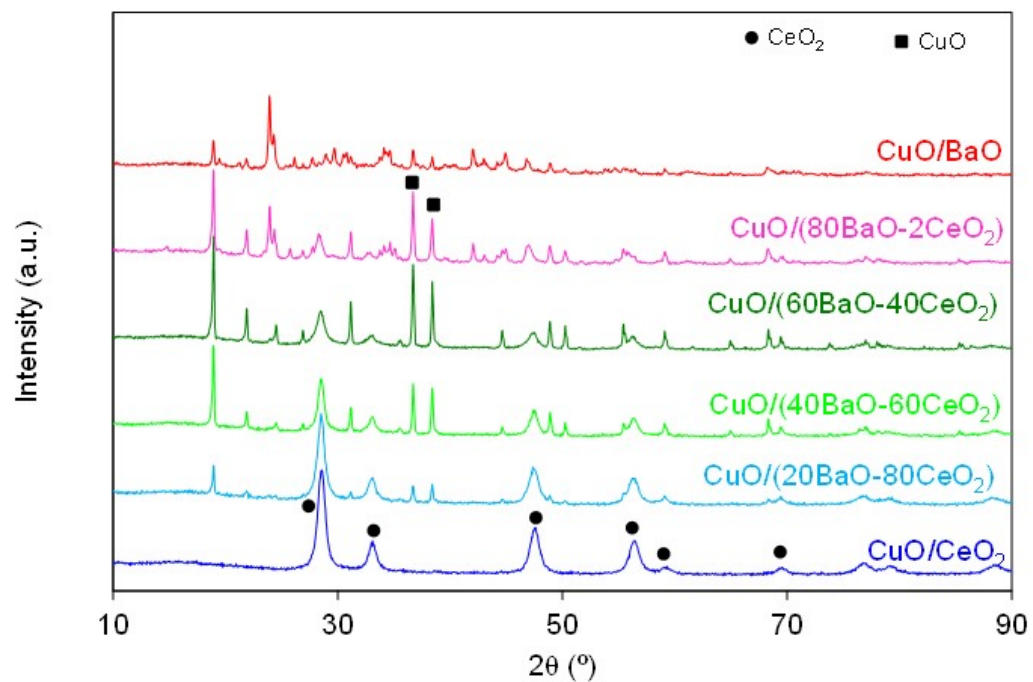
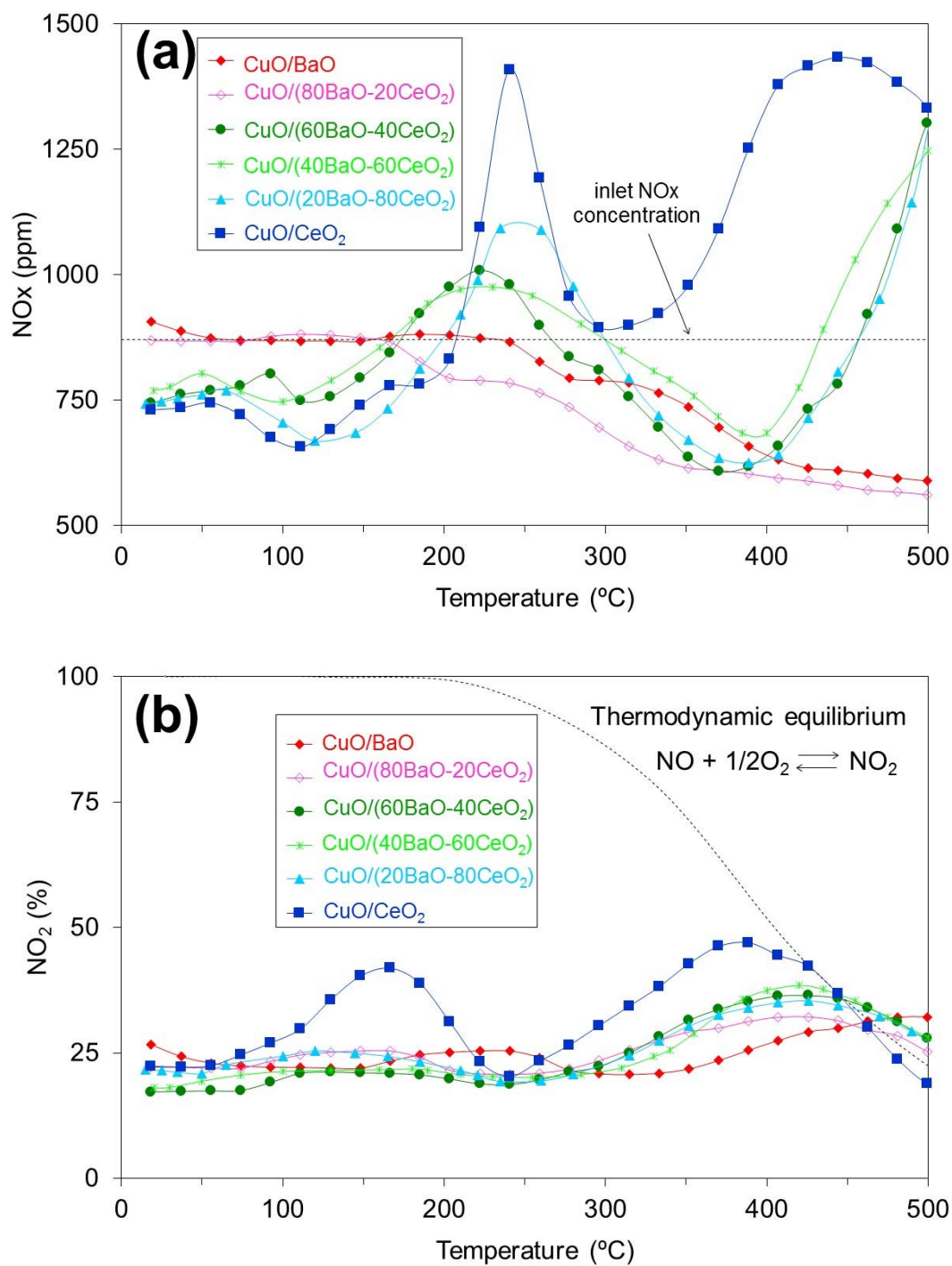
Figure 1

Figure 2

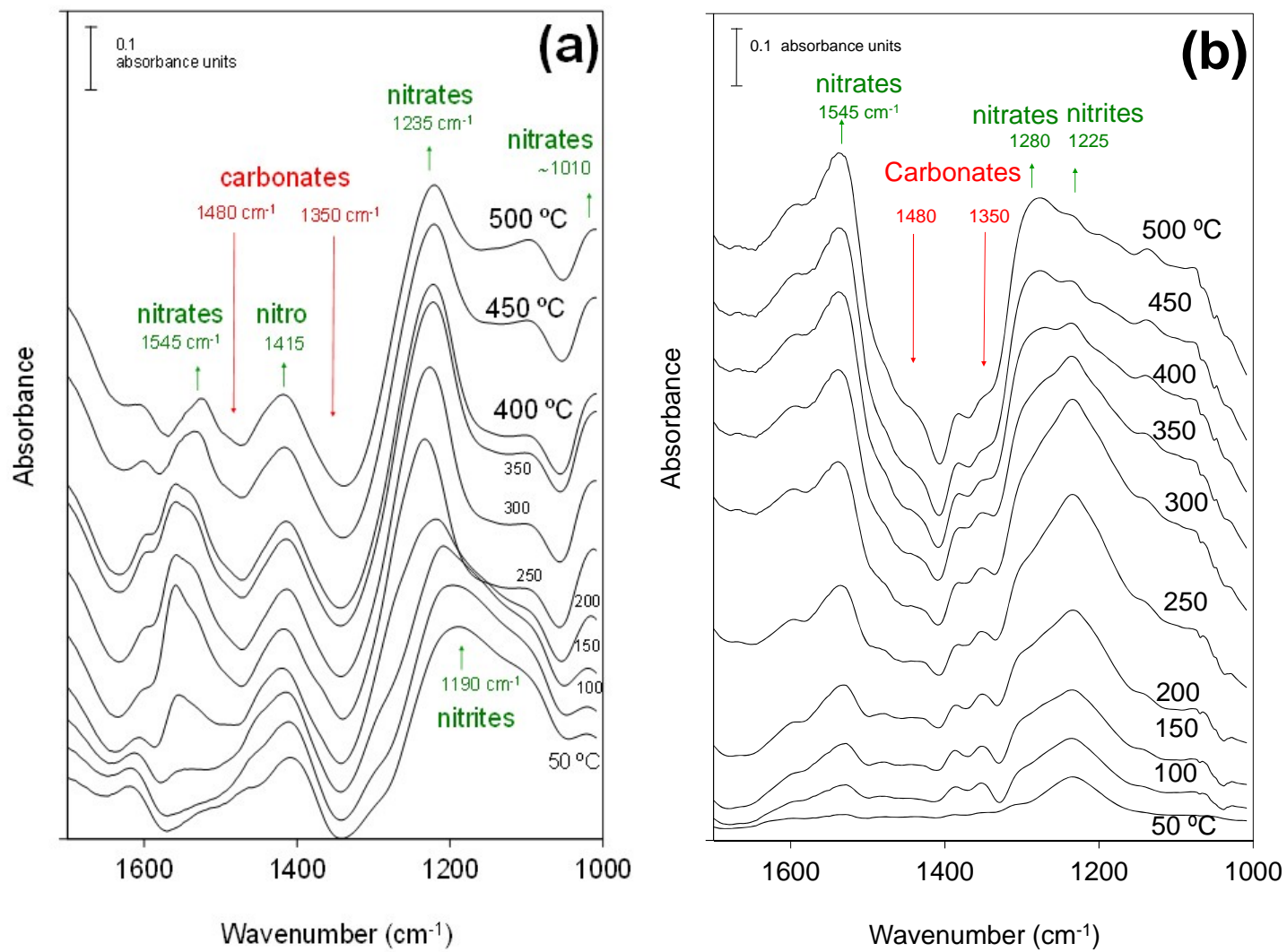
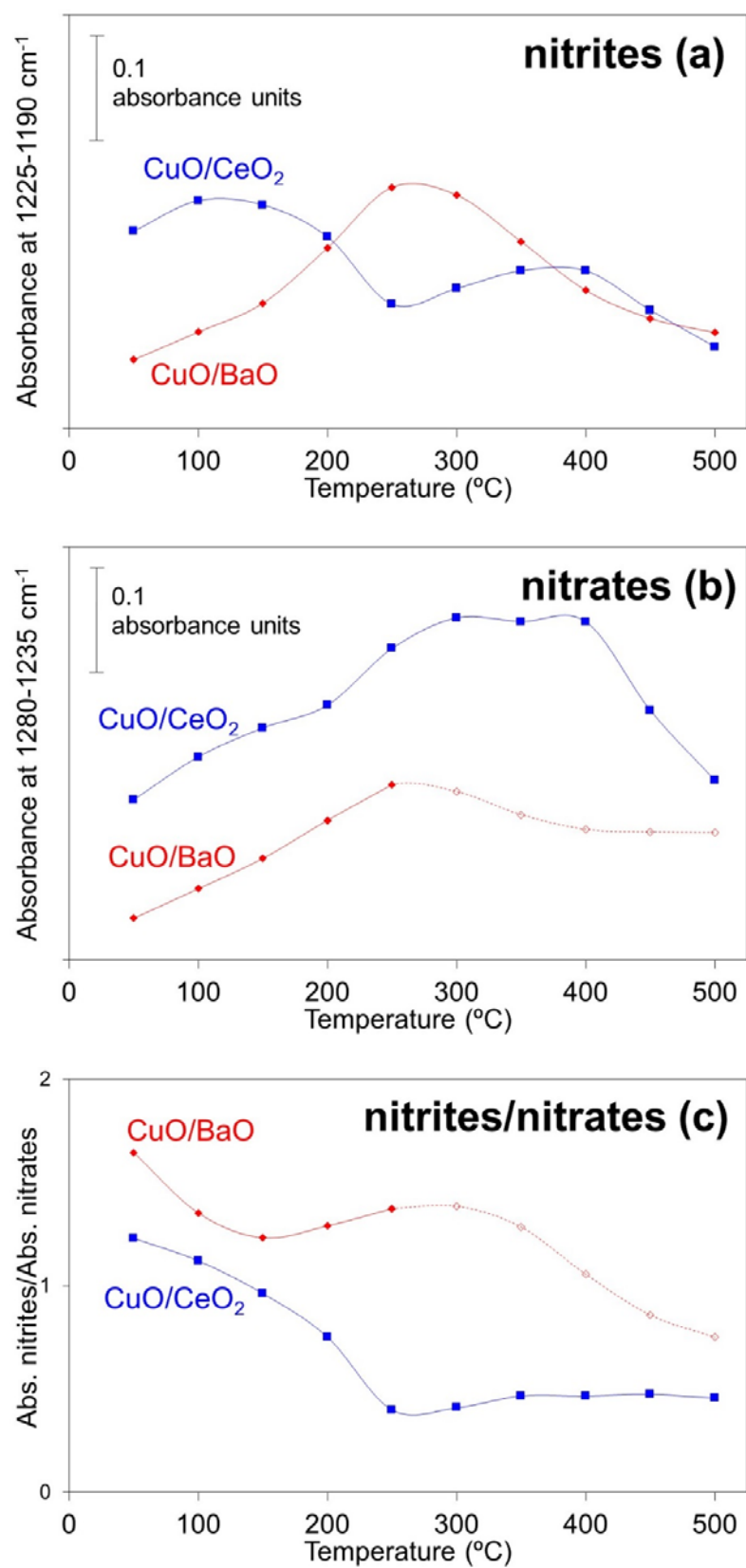
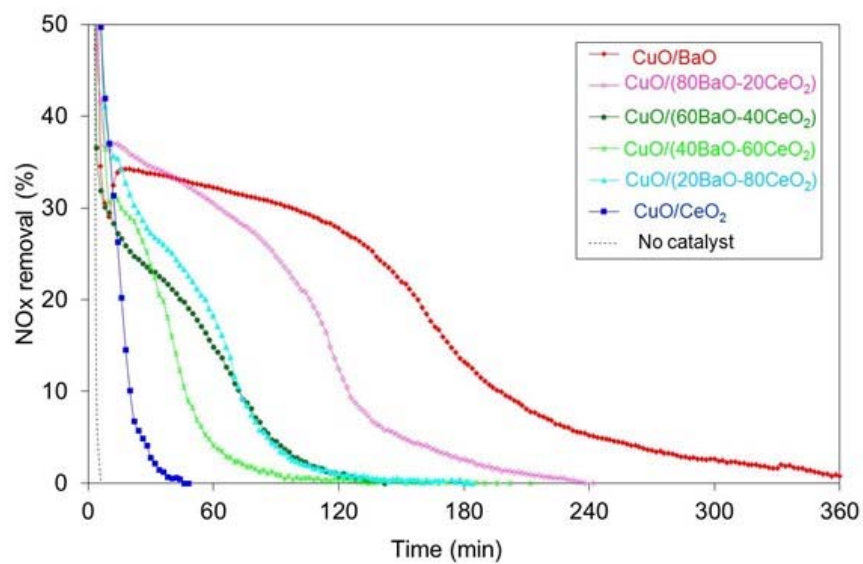


Figure 3

**Figure 4**

**Figure 5**

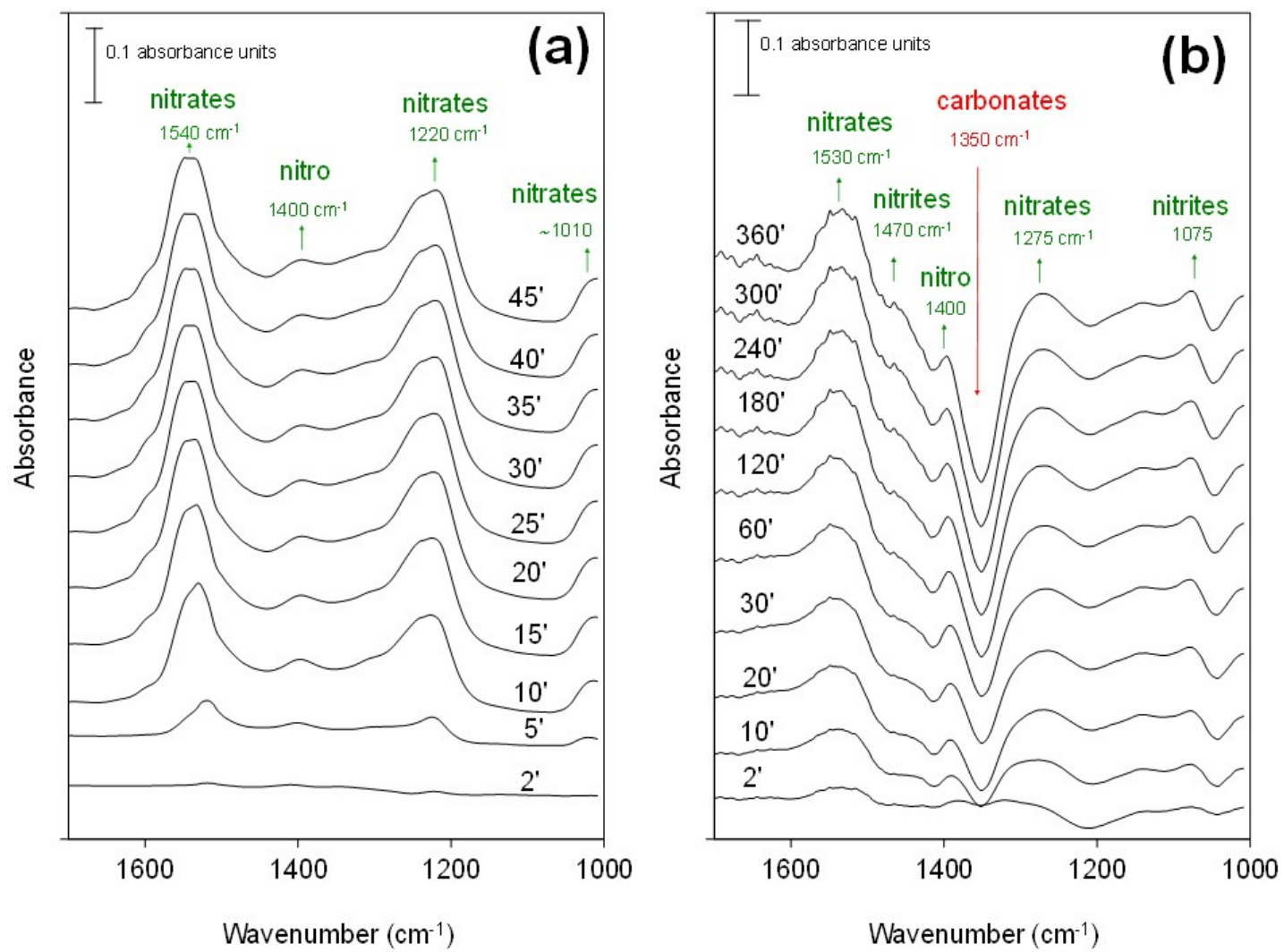
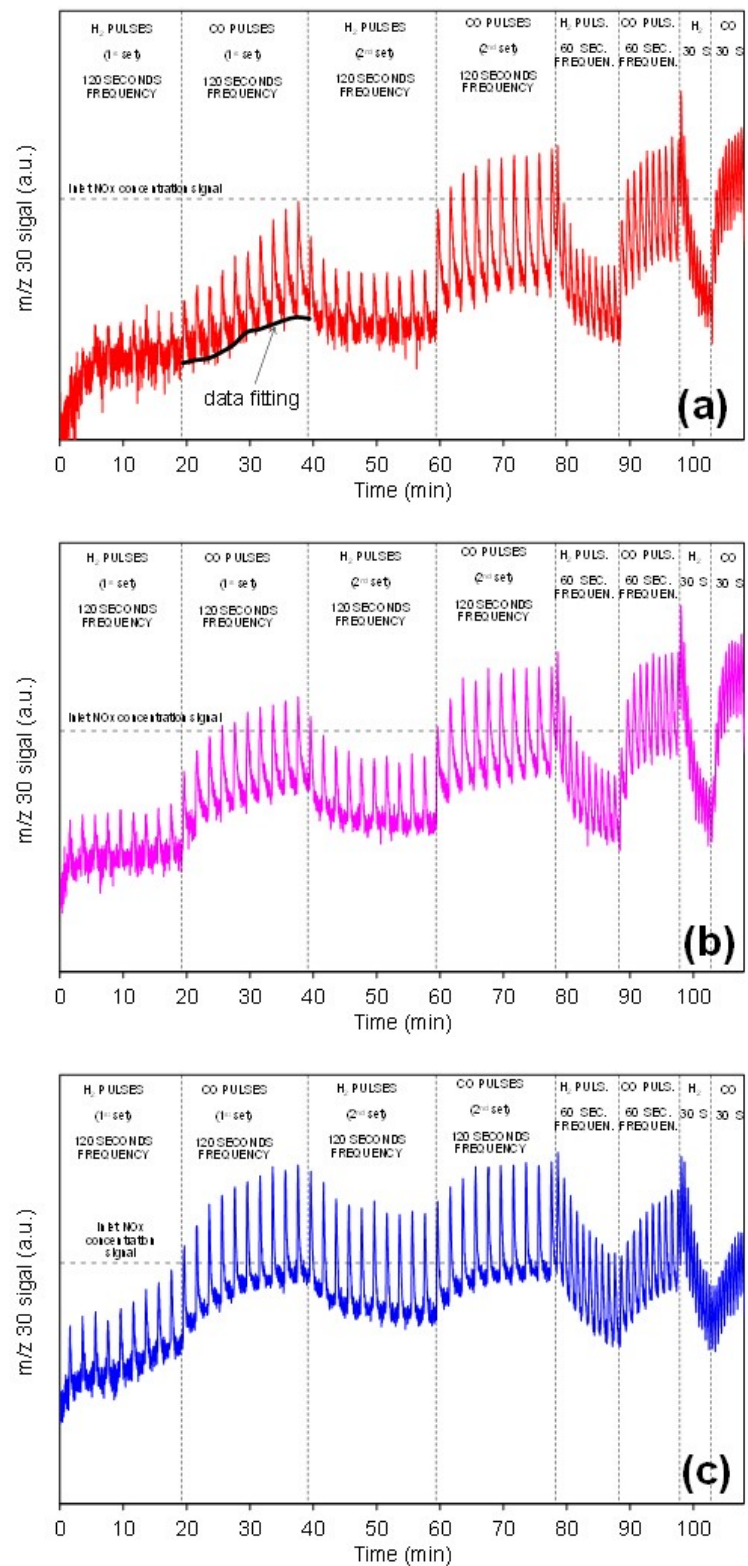
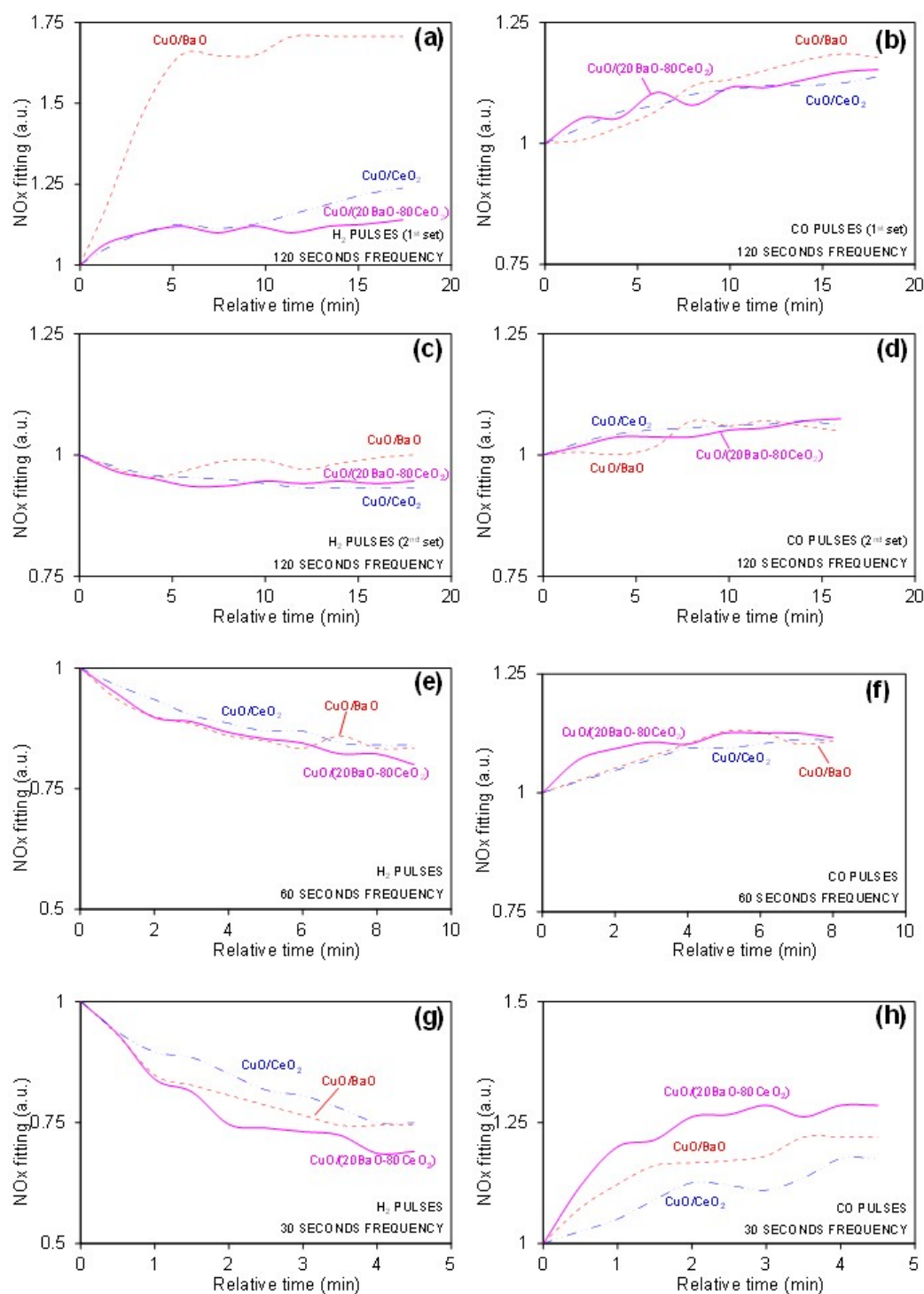


Figure 6

**Figure 7**

**Figure 8**

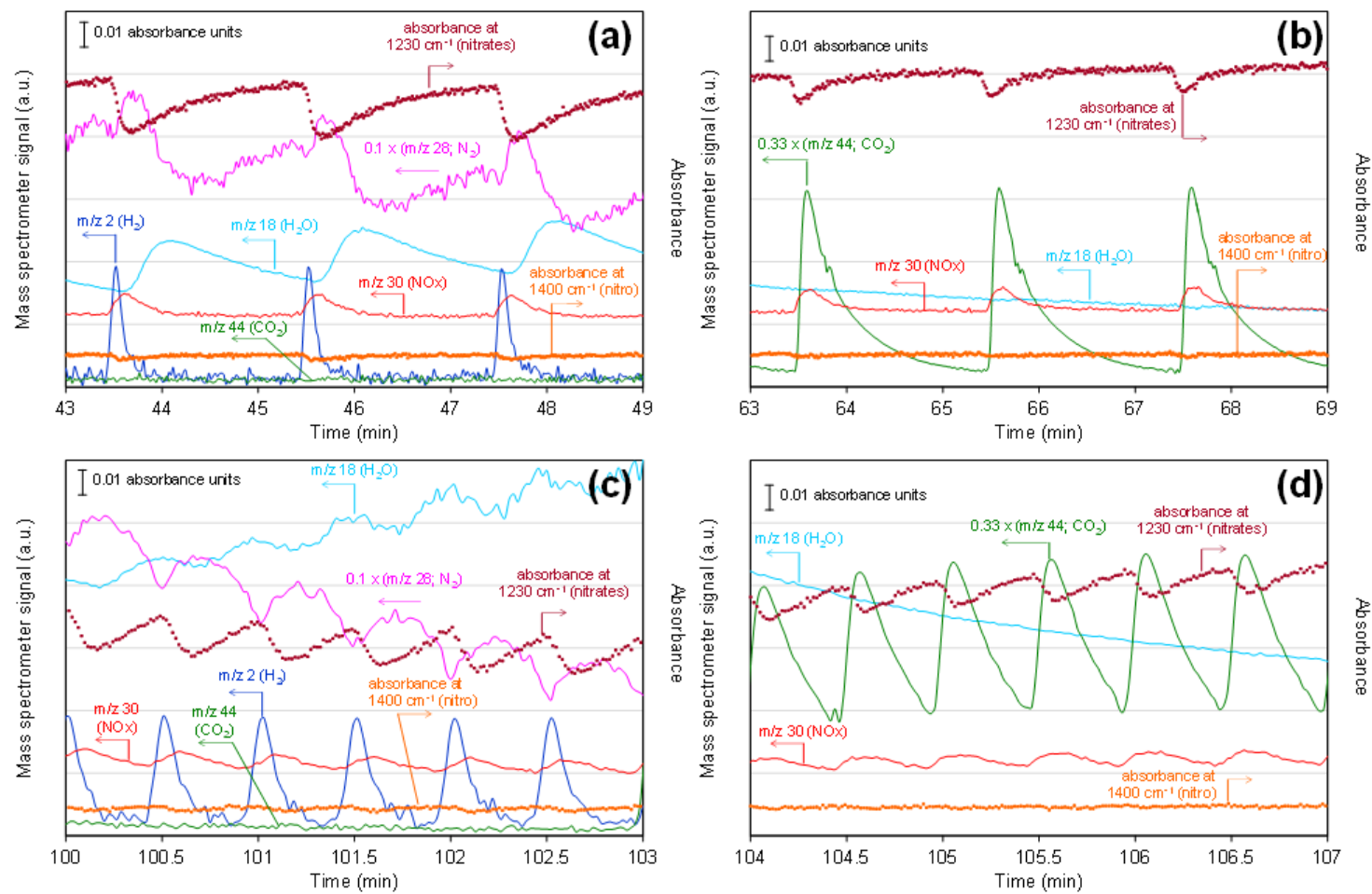


Figure 9

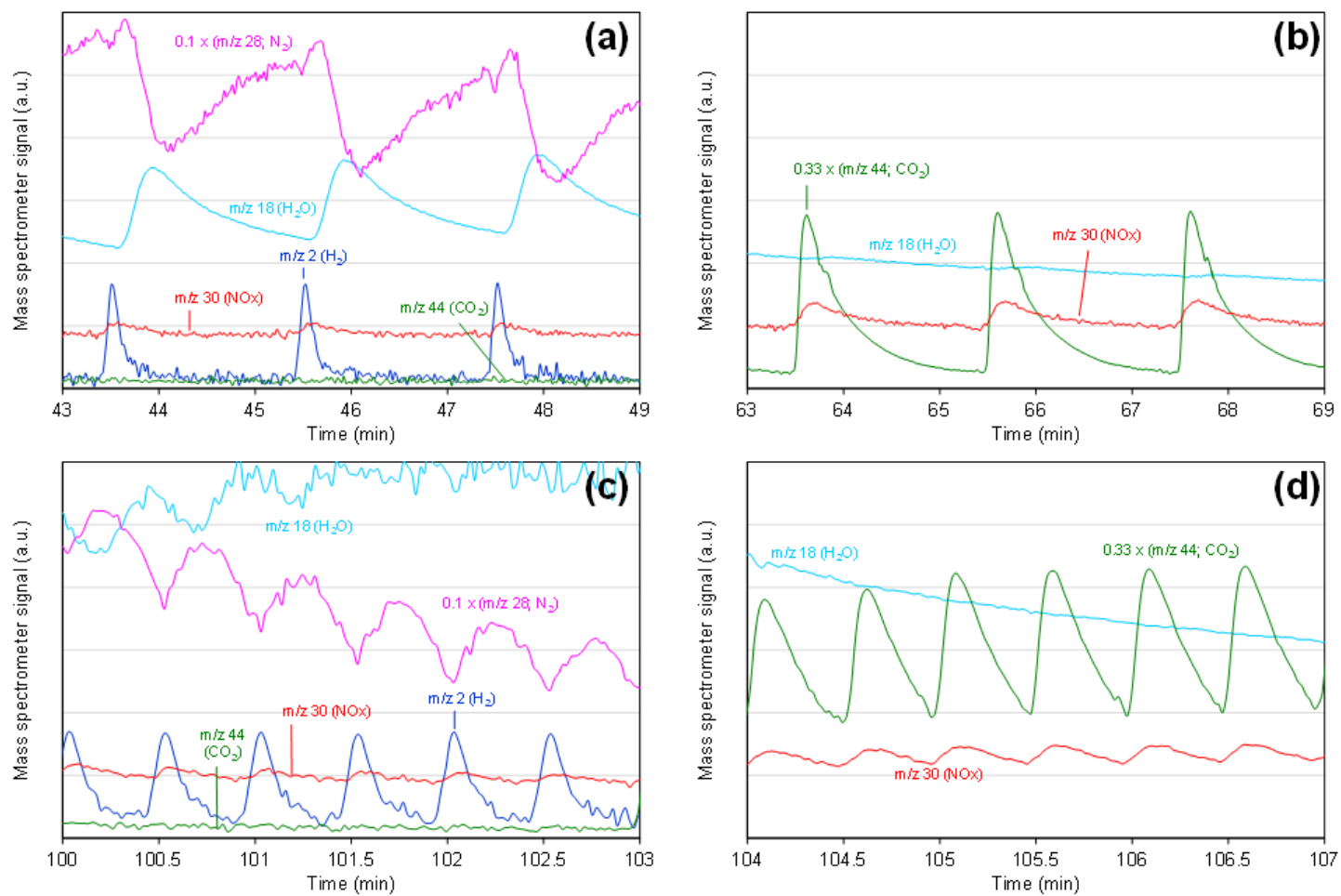


Figure 10

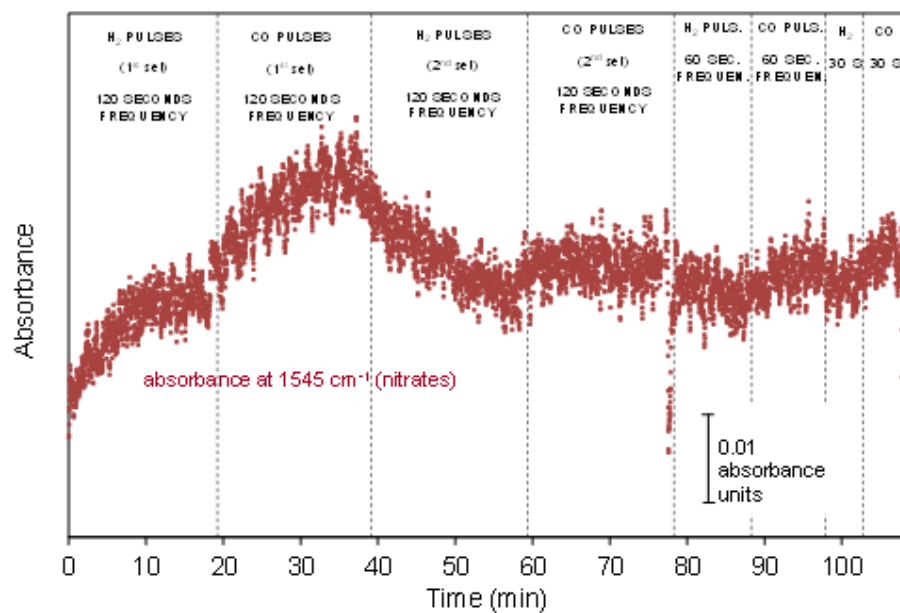


Figure 11

Table 1. BET surface area of the catalysts and fluorite cell parameter.

Catalyst	BET (m ² /g)	Fluorite cell parameter (nm)
CuO/CeO ₂	60	0.5411
CuO/(20BaO-80CeO ₂)	30	0.5414
CuO/(40BaO-60CeO ₂)	11	0.5420
CuO/(60BaO-40CeO ₂)	13	0.5420
CuO/(80BaO-20CeO ₂)	1	0.5429
CuO/BaO	1	-

Table 2. Amount of NO_x stored on the catalysts at 400°C.

	NO _x stored at 400°C (μmolNO _x /g _{catalyst})
CuO/CeO ₂	168
CuO/(20BaO-80CeO ₂)	437
CuO/(40BaO-60CeO ₂)	281
CuO/(60BaO-40CeO ₂)	343
CuO/(80BaO-20CeO ₂)	779
CuO/BaO	1204